

DRAWINGS ATTACHED.

971,943



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## COMPLETE SPECIFICATION.

## Improvements in and relating to Mineral Active Carbons and to a Process for Their Preparation.

## SPECIFICATION NO. 971,943

By a direction given under Section 17(1) of the Patents Act 1949 this application proceeded in the name of NILOK CHEMICALS, INC., a Corporation organised and existing under the laws of the State of New York, United States of America, of Mill Street and North Transit Road, Lockport, New York, 14094, United States of America.

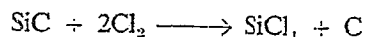
THE PATENT OFFICE

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15 This invention relates to mineral active carbons and to a process for their preparation.

Active carbons have previously been prepared by the charring or carbonisation of organic substances, usually followed or accompanied by a process of controlled oxidation known as activation. Choice of organic starting material and numerous modifications of the process have been used to prepare a large variety of such organic active carbons suited to a variety of end uses.

25 The production of silicon tetrachloride by the reaction :—



30 at temperatures above 1000° C. was disclosed by Hutchins in 1918 (U.S. Patent No. 1,271,713) and the commercial production of silicon tetrachloride by this reaction is well known to the art. Lower reaction temperatures of about 800—900° C. are preferred in order to simplify construction and operation of the equipment but at these lower temperatures, once the surface of the silicon carbide particle has been converted to a layer of carbon, the reaction proceeds too slowly to be completely satisfactory.

[Price 4s. 6d.]

carbides or carbonitrides of metals or metalloids having volatile chlorides can be chlorinated to produce the corresponding chloride and to leave a carbon residue which, when dechlorinated, is a highly adsorbent active carbon. 55

By means of the present invention it is possible to produce active carbon and metal or metalloid chlorides simultaneously, thereby effecting economies as compared to preparation separately of either active carbon or metal (metalloid) chlorides by methods which are presently known to the art. 60

It is also possible to prepare active carbon from inorganic raw materials, namely metal carbides or metalloid carbides, which can be made available in unlimited quantities, which are domestically available, and which are essentially uniform in quality. 65 70

It is also possible to produce active carbon by a process which does not use, nor require, gas activation processes such as high temperature oxidation with steam or with carbon dioxide, and which does not use activating chemicals such as calcium, magnesium or zinc chlorides, alkali metal sulphates, phosphoric acid, caustic soda or potash, sulphides, thiocyanates, or similar chemicals. 75

It is also possible according to this inven- 80

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## COMPLETE SPECIFICATION.

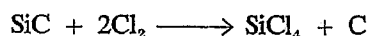
### Improvements in and relating to Mineral Active Carbons and to a Process for Their Preparation.

I, GORDON OWEN SHIPTON, a British Subject, of 12 Church Street, Liverpool 1, Lancashire, do hereby declare the invention (a communication from NILOK CHEMICALS, INC., a Corporation of the State of New York, United States of America, of 2000 College Avenue, Niagara Falls, New York, United States of America), for which I pray that a patent may be granted to me, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to mineral active carbons and to a process for their preparation.

Active carbons have previously been prepared by the charring or carbonisation of organic substances, usually followed or accompanied by a process of controlled oxidation known as activation. Choice of organic starting material and numerous modifications of the process have been used to prepare a large variety of such organic active carbons suited to a variety of end uses.

The production of silicon tetrachloride by the reaction:—



at temperatures above 1000° C. was disclosed by Hutchins in 1918 (U.S. Patent No. 1,271,713) and the commercial production of silicon tetrachloride by this reaction is well known to the art. Lower reaction temperatures of about 800—900° C. are preferred in order to simplify construction and operation of the equipment but at these lower temperatures, once the surface of the silicon carbide particle has been converted to a layer of carbon, the reaction proceeds too slowly to be completely satisfactory.

[Price 4s. 6d.]

Anderson (U.S. Patent No. 2,739,041) has disclosed a process in which periods of chlorination are alternated with periods in which air is blown into the hot reactor to remove the carbon by combustion. In the present state of the art the carbon is always burned off or, still saturated with chlorine, is discarded as waste. Hutchins disclosed that the carbon residue is in the form of graphite—a form of carbon which is not surface active.

It has now been discovered that the carbides or carbonitrides of metals or metalloids having volatile chlorides can be chlorinated to produce the corresponding chloride and to leave a carbon residue which, when dechlorinated, is a highly adsorbent active carbon.

By means of the present invention it is possible to produce active carbon and metal or metalloid chlorides simultaneously, thereby effecting economies as compared to preparation separately of either active carbon or metal (metalloid) chlorides by methods which are presently known to the art.

It is also possible to prepare active carbon from inorganic raw materials, namely metal carbides or metalloid carbides, which can be made available in unlimited quantities, which are domestically available, and which are essentially uniform in quality.

It is also possible to produce active carbon by a process which does not use, nor require, gas activation processes such as high temperature oxidation with steam or with carbon dioxide, and which does not use activating chemicals such as calcium, magnesium or zinc chlorides, alkali metal sulphates, phosphoric acid, caustic soda or potash, sulphides, thiocyanates, or similar chemicals.

It is also possible according to this inven-

tion to produce directly an active carbon with low ash content without the necessity of separate ash removing processes, and to produce a carbon which is neutral in aqueous suspension. Further, it is possible to produce an active carbon in granular form suitable for gas adsorption uses or to produce a pulverized carbon suitable for liquid phase applications.

Finally it is possible according to this invention to produce, as a new composition of matter, a carbon having properties, physical form, and structure differing from those previously known to the art.

For convenient reference throughout this Specification and claim, the active carbons previously known to the art, formed by the carbonization of organic matter, will be called "organic active carbons"; and the novel active carbon of the present invention, prepared from inorganic matter, will be called "mineral active carbon".

According to the present invention therefore there is provided dechlorinated mineral active carbon containing no bound hydrogen.

The invention also includes a process for the preparation of dechlorinated mineral active carbon containing no bound hydrogen which comprises chlorinating, at an elevated temperature, a carbide or carbonitride of a metal or metalloid whose chloride is volatile at the elevated temperature, volatilising and removing the resultant chloride from the reaction mass and dechlorinating the residual carbon.

Commercially common examples of metals or metalloids whose carbides or carbonitrides may be used are aluminium, boron, silicon, titanium and zirconium.

Figure 1 of the accompanying drawings is an optical photomicrograph at 330 $\times$  magnification showing the laminated structure of a typical mineral active carbon according to the invention.

Figures 2 and 3 of the accompanying drawings are electron photomicrographs at 37350 $\times$  magnification showing the lamellar fine structure of a typical mineral active carbon, Figure 3 being an edge view of the lamellae and Figure 2 being a flat view.

It has been found that mineral active carbon prepared without any special activation procedures such as are frequently employed in making organic active carbons has gas adsorption and organic vapour adsorption properties comparable to, or superior to, gas-activated organic carbons presently offered commercially for these purposes. It also has adsorption properties in aqueous systems comparable to, or superior to, commercial decolorizing organic active carbons.

Only about one commercial activated carbon type in four has an inorganic ash content less than 2% by weight and only about one in ten has an ash content below 1%.

Ash contents in the range 1—2% may conveniently be referred to as "low" and those below 1% as "very low". It has been found that the inorganic ash present in mineral active carbons forms a mineral skeleton holding the carbon granule together. Since the hardness and attrition resistance of the carbon granules depend upon the nature and quantity of the ash content, a low ash content is not always desirable. But when end use requires a carbon with ash in the "low" or "very low" range, it has been discovered that mineral active carbon can be prepared in these grades. It has also been found that mineral active carbon can be produced in a grade which is essentially neutral in aqueous suspension.

Dechlorination of the residual carbon according to the process of the invention, for example, by sweeping the reactor with inert gas during cooling or by dechlorination of the cool chlorine-saturated carbon, is an essential step because the product cannot be surface active until the chlorine which is present in situ during its formation is removed. Furthermore, the carbon should preferably be dechlorinated before it is exposed to moist air because such moisture will react with the chlorine on the carbon forming hydrochloric acid which would also be adsorbed and which would make the carbon difficult to handle and useless for practical purposes until it, in turn, was removed.

The necessary conditions for the chlorination reaction are to provide enough heat to get the reaction started and then, since the reaction is exothermic, to dissipate the heat released by the reaction. Any suitable form of apparatus may be employed utilising either a static or fluidized bed according to engineering principles which are known in the art. Since reaction rates increase with increasing temperature and since this in turn raises the temperature further, there is a tendency for the reaction to "run away". Fortunately close temperature control is not essential and the rate of reaction can be held in check by controlling the rate at which chlorine is made available to the reaction zone, as for example by throttling the chlorine feed rate or by diluting the chlorine with an inert gas. For the same reasons, there is a tendency for the reaction to run away in localized regions of the reaction zone forming hot spots which migrate through the bed. Such high temperatures favour formation of a turbostratic or a graphite structure, neither of which are adsorbent. Control of the hot spots by controlling the rate of feed is essential. In order to reduce the hot spots additional gas may be passed through the reaction zone to carry heat away from the hot spots. This additional gas may be either an inert diluent gas mentioned above or merely additional chlorine. Temperatures in

the range 900° C. to 1200° C. are considered optimum for chlorinating silicon carbide from the standpoint of maximum adsorptive power of the carbon, but various adsorptive powers are commonly employed for varied uses so that engineering convenience and economy may dictate any choice of temperature in the range 800° C. to 1800° C. depending upon the type of apparatus employed. Titanium, zirconium, aluminium, and boron carbides, and zirconium and titanium carbonitrides all react readily at temperatures below those necessary for silicon carbide so that less refractory materials may be used for the reaction chamber and temperature control is facilitated.

Any convenient chlorine feed rate may be used which meets the needs of temperature control. Where the gas used for reducing hot spots is additional chlorine then, after removing the volatile chloride, the excess chlorine may be recycled or used for other purposes. If the reaction zone is a fluidized bed, then the chlorine rate, with or without diluent, must also meet the physical requirements of fluidization control. Fluidization, of course, greatly improves heat transfer and eliminates hot spots. At the lower operating temperatures hot spots are not likely to be a problem. When troublesome they can be eliminated by equipment design alone but suitable heat dispersal by gas flow may preferably be combined with other design features to meet the desired objectives.

Although many metal or metalloid carbides or carbonitrides may suitably be used as raw material, silicon carbide has been selected to illustrate the novel process of the present invention in detail. Any silicon carbide raw material may be used. Low quality grades such as firesand will result in a lower quality carbon containing considerable silica, but for some purposes this may not be undesirable. The principal impurities in silicon carbide are carbon, elemental silicon, silica, calcium, iron and alumina. In the chlorination process the silicon and silica are converted to silicon tetrachloride; the iron, and some of the alumina are converted to chlorides which are volatile at the reaction temperature and are thus removed from the reaction zone. These metal chloride impurities are readily removed from the silicon tetrachloride co-product by conventional means. Abrasive grade black silicon carbide contains very little carbon and silica and is an eminently suitable raw material for the process. Green silicon carbide is an even purer starting material yielding maximum purity of product.

Any convenient size of silicon carbide can be used. There have been used abrasive grit numbers 8 to 240 in static beds and even finer sizes may be used in fluidized beds. If the particles are too large the time for

complete reaction is unduly prolonged, but since crude silicon carbide contains few crystals which are much coarser than 8 mesh only a simple crushing to break apart the friable crude mass is needed. Since the size of the silicon carbide crystal substantially determines the size of the carbon particle, the size of silicon carbide selected will be considerably influenced by the size of carbon particle which is desired.

There is a tendency for an unreacted core of silicon carbide to remain at the centre of the carbon particle due to the slow diffusion of chlorine into, and the slow diffusion of silicon tetrachloride out of, the inner part of the reacting particle. Both diffusion and reaction are accelerated by increased temperature and it has been found that operating temperatures in excess of 1000° C. are beneficial in eliminating unreacted cores. For this reason hot spots are beneficial provided that they are not excessive. Any cyclic change in reactor temperature or pressure will expedite diffusion by causing the particles to "breathe"; rising temperatures or falling pressures drive the silicon tetrachloride product vapours out of the interior of the particle while during the other half of the cycle falling temperatures or rising pressures pull the chlorine reactant into the particle to the unreacted silicon carbide core. Since hot spots represent regions of abnormal temperature change they tend to contribute in this way too, to complete reaction of the core. Changes in reactor pressure are readily provided by valving the inlet and outlet gases of the system.

When some inert silicon carbide core in the carbon particle is not objectionable, as for example when the carbon is to be used at a catalyst support, the reaction time may economically be shortened somewhat. Further, when the carbon is to be used as a fine powder, unreacted silicon carbide can be separated from it in a subsequent mechanical process; the relatively friable carbon is broken away from the hard silicon carbide core by a mild pulverizing action and the two components of different density and size may be separated by any convenient means known to the art such as by screening or by fluid medium separation processes.

The silicon tetrachloride formed in the reaction passes out of the reaction chamber, is condensed, and purified by known means. Because silicon tetrachloride reacts extremely readily with moisture, forming silica and hydrochloric acid, moisture must be carefully excluded from the process. Commercial chlorine may contain traces of moisture which, reacting with the silicon tetrachloride within the carbon particle, precipitates some silica in the carbon. Although commercial chlorine is found satisfactory it may be desirable to dry it under special circum-

stances where considerable excess chlorine is being used or where an extremely pure product is required.

5 At the end of the chlorination operation the carbon is saturated with calcium at the reaction temperature and, as disclosed above, this chlorine must be removed before a useful active carbon can be obtained. Dechlorination may be accomplished in any of several ways. 10 Thus, for example, the carbon may be cooled from the reaction temperature in an atmosphere of chlorine and may subsequently be dechlorinated; or an inert gas, as for example nitrogen or argon, may be introduced into 15 the reaction vessel, to sweep out the chlorine, at any stage of the cooling period. At room temperature, essentially all of the chlorine will be removed by the inert gas stream at atmospheric pressure. The duration of the 20 dechlorination operation depends upon the temperature and the pressure; sub-atmospheric pressures will favour lower temperatures or shorter times. For rapid and complete dechlorination at atmospheric pressure 25 a temperature of 150° C. with a moving gas stream is satisfactory. When the dechlorination is carried out at temperatures below the combustion temperature of the carbon, it is quite satisfactory to employ a stream of air, 30 preferably dried, instead of the inert gas. Or a stream of steam may be employed at temperatures high enough to avoid condensation in the carbon and low enough to avoid oxidation of the carbon. Carbon dioxide 35 may be used at temperatures low enough to avoid oxidation of the carbon.

Of considerable importance is the silicon tetrachloride which remains trapped in the carbon when the reaction is complete, since 40 upon exposure to the air it hydrolyzes depositing silica and hydrochloric acid in the carbon and adversely effects the adsorptive power of the carbon. This silicon tetrachloride may, or may not, all be removed 45 by the dechlorination process. In any event the silicon tetrachloride must be removed before exposure to the air, if its hydrolysis is to be avoided, whereas dechlorination is not so limited. The silicon tetrachloride is 50 readily removed by any cyclic fluctuation in temperature or pressure which causes the carbon particle to breathe while gas is passed through the vessel to sweep away the silicon tetrachloride; such processes are here referred to as "purging". The gas employed 55 for purging may be either chlorine or an inert gas such as nitrogen or argon, or, when operating at temperatures below those at which combustion occurs, dry air may be used. Any convenient temperature may be 60 employed for this purging operation from room temperature to temperatures in excess of the reaction temperature. If carried out at the same time as dechlorination, such

purging cycles assist in removing the chlorine too. 65

Dechlorination may also be carried out by heating, without a gas stream, thin layers of carbon at a temperature of 100° C. or higher, but preferably in the range 200— 70 300° C.

If the carbon has been cooled in an atmosphere of chlorine, or if the cooling has occurred in the presence of an inert gas or air but in such a way that the dechlorination is incomplete, the carbon may be dechlorinated by one of the processes described above or by one of the wet processes described below, or by any convenient combination of them. Dechlorination may be carried out 75 by washing the carbon with water. Dechlorination may be carried out by washing in alkaline solution such as aqueous caustic soda, sodium bicarbonate, or ammonia, followed by water washing, with or without 80 acid neutralization of residual alkaline solution and final water washing. Dechlorination may be effected by treating the carbon with aqueous reducing agents such as thiosulphate, hyposulphite, bisulphite, or hydrogen 85 peroxide followed in each case by water washing, with or without destroying the excess reducing agent by addition of a suitable oxidising agent followed by final washing.

At the end of the chlorination operation 95 chloride molecular species of undetermined composition, other than silicon tetrachloride, may be present in the carbon. These are probably sub-chlorides of silicon and/or of carbon. Carbons made without special precautions to remove the residual chlorides 100 from the carbon have a pH in aqueous suspension of about 2 to 3. These acidic mineral active carbons have excellent adsorption properties and may be used for many purposes. The mineral active carbon, if desired, 105 may be brought to within about one pH unit of neutrality by any of the wet dechlorination methods described in the preceding paragraph, except by thiosulphate or by 110 hyposulphite. pH is also raised, and chloride is removed from the carbon, by heating in an inert gas stream; the temperature employed depends upon the amount of improvement 115 desired in the purity of the mineral active carbon, temperatures in excess of 250° C. usually being preferred. This purification operation may readily be combined with 120 dechlorination by a heated gas stream by prolonging the treatment time beyond that required for dechlorination only and it may take the form of a purging operation using cyclic temperature or pressure variations. Any suitable gas may be employed which is 125 inert at the temperature in question, as for example nitrogen or air. Such a purification of the carbon substantially improves its adsorptive power.

The chlorination step can be carried out

as a batch process, as a continuous process or as a semi-continuous process with intermittent feed and/or discharge. Dechlorination and/or purging and/or purification using a gas stream may be combined with these chlorination operations in the same or in subsequent vessels. Either static or fluidized beds may be used.

Although the foregoing detailed exposition of the process of the present invention has been described for the case of silicon carbide raw material, these principles may be applied to any metal or metalloid carbide or carbonitride whose chloride is volatile at the temperatures employed, by changes in accordance with the specific characteristics of the metal or metalloid in question which will be apparent to those skilled in the art, as for example changes in the temperature at which the chlorination may be carried out for metals or metalloids of differing reactivity.

Although the disclosed processes produce excellent mineral active carbon suitable for a great variety of uses, known processes of adding trace metals to the finished active carbon, as for example silver, copper, or manganese, may advantageously be applied to mineral active carbon for applications where these additions are known in the art to be desirable, such as for carbons to be used in gas mask canisters.

Various finishing operations, such as pulverizing or pelletizing to bring the mineral active carbon to a state of sub-division suitable for specific end-use circumstances, may advantageously be employed. Pelletizing, with or without a binder, may be carried out by any of the processes known to the art, some of which employ a heating operation to carbonize the binder.

The number of end-use applications for which active carbon is employed is very large and somewhat different properties are required in different active carbons for different purposes. The invention embraces not a single mineral active carbon product but a range of carbons of varying properties obtained by combining in any suitable way the novel inventive processes disclosed herein with or without the conventional processes of upgrading chars which are known to the art.

The following examples illustrate various ways of carrying out the processes of the invention and illustrate the properties of the novel mineral active carbon products produced thereby; these examples are solely for purposes of illustration and are not intended to limit in any way the broad scope of our invention.

#### EXAMPLE No. 1.

About 23 grams of abrasive grade 16 grit green silicon carbide (nominally 99.5% SiC) were placed in a porcelain boat in a silica tube heated externally with silicon-carbide-

type electric resistance heaters and chlorine was passed through the tube at a rate of about 0.5 gram per minute for 520 minutes while maintaining a temperature of 950° C. The product was cooled and dechlorinated in a stream of dry, oxygen-free nitrogen. The resulting carbon product contained 44.6% ash which was largely unreacted silicon carbide, corresponding to about 80% completion of the chlorination reaction. In an adsorption tube supplied with chlorine gas 2.265 grams of the product adsorbed 0.837 gram of chlorine at 30° C., which corresponds to 0.67 gram of chlorine adsorbed per gram of carbon in the product. When 0.500 gram of the product was shaken with an aqueous iodine-potassium iodide solution for forty minutes it adsorbed 0.356 gram of iodide.

#### EXAMPLE No. 2.

172.5 grams of abrasive grade 30 grit green silicon carbide (nominally 99.5% SiC) were placed in a one inch diameter mullite tube provided with an external electric heater and chlorine was passed through the tube at a rate of 10 to 18 grams per minute while maintaining a nominal temperature of 1000° C. Actual temperature was in excess of 900° C. for eleven and three quarters hours of which four hours was in excess of 1050° C. the maximum temperature reached was 1175° C. The contents of the tube were cooled to below 200° C. under a stream of nitrogen. The product was removed and held at 100° C. in a laboratory oven over the weekend. The product contained 27.2% ash, mostly unreacted silicon carbide, which corresponds to 90% completion of the chlorination reaction. At 30° C. the product adsorbed 0.437 gram of chlorine per gram of product which is about 0.60 gram of chlorine per gram of contained mineral active carbon. A sample of the product ground through 100 mesh adsorbed, from an aqueous iodine-potassium iodide solution, 0.57 gram of iodine per gram of product. When 0.50 gram of the minus 100 mesh product was shaken for 60 minutes with 75 ml. of aqueous solution containing 50 milligrams of methylene blue, 51% of the methylene blue was adsorbed by the mineral active carbon, that is, 0.051 gram of methylene blue was adsorbed per gram of product.

#### EXAMPLE No. 3.

100 grams of abrasive grade 16 grit black silicon carbide (nominally 99% SiC) were placed in a one inch diameter mullite tube provided with an external electric heater and chlorine was passed through the tube at a rate of 9.5 to 11 grams per minute while maintaining a nominal temperature of 1050° C. Actual temperature was in excess of 800° C. for periods of time totalling forty hours of which thirty-one hours were in the 1000° C. to 1100° C. range; temperature

occasionally rose above 1100° C. for a few minutes due to hot spots, the maximum temperature recorded during the chlorination being 1160° C. Heating and cooling periods due to three interruptions in the operation account for the time at temperatures below 1000° C. The silicon tetrachloride produced in the reaction was determined by passing the gases emerging from the tube into water whereby the silicon tetrachloride was converted to silicic acid. Essentially all of the aluminium chloride and iron chloride, which sublimed out of the reaction mass, condensed in the tubing and were thereby separated from the silicon tetrachloride. 136 grams of silica was recovered by evaporating the aqueous silicic acid and dehydrating at 1400 C.; this corresponds to 385 grams of silicon tetrachloride which is 91% of theoretical. After cooling in an atmosphere of chlorine the carbon residue left in the mullite tube was dechlorinated by heating in a laboratory oven for 8 hours at 120° C. The weight of carbon recovered was 27.5 grams which is 92% theoretical. This carbon contained 1.3% ash which showed no visible traces of unreacted silicon carbide; this mineral active carbon adsorbed from an aqueous iodine-potassium iodide solution 0.84 gram of iodine per gram of contained carbon. Under the same test conditions a commercial sample of decolorizing carbon (Norbit FPQ) adsorbed 0.75 gram of iodine per gram of sample. This mineral active carbon adsorbed 0.63 gram of chlorine per gram of contained carbon.

#### EXAMPLE No. 4.

(Green Silicon Carbide, Cooled in Nitrogen, Low Ash, Good Adsorption).

About 23 grams of abrasive grade 30 grit green silicon carbide (nominally 99.5% SiC) were placed in a porcelain boat in a one inch diameter silica tube provided with an external electric heater and chlorine was passed through the tube at a rate of about 0.465 gram per minute, while maintaining a temperature of 1000° C. at a thermocouple in a Vycor protection tube in the gas stream just above the boat, for a total of 635 minutes. Oxygen-free, thoroughly-dried nitrogen was used to sweep out the tube (a) before the chlorination while the tube was being raised to temperature, and (b) after the chlorination while the tube was cooling to below 500° C. The silicon tetrachloride produced was condensed in a tube cooled in ice. The resulting mineral active carbon contained 0.08% ash. Upon pumping under vacuum for 30 minutes at 150° C. the mineral active carbon lost 6% in weight and then was able to adsorb 0.636 gram of chlorine per gram of carbon at 30° C. This sample of mineral active carbon adsorbed

0.831 gram of iodine per gram of carbon from aqueous iodine-potassium iodide solution; it adsorbed 0.038 gram of methylene blue per gram of unground carbon.

#### EXAMPLE No. 5.

(For photomicrograph at 330× magnification showing laminated structure i.e. Figure 1).

100 grams of abrasive grade 16 grit black silicon carbide (nominally 99% SiC) were chlorinated, using chlorine which had been dried by bubbling through sulphuric acid, with a flow rate of about 10 grams of chlorine per minute while maintaining a nominal temperature of 1050° C. Actual temperature was in excess of 800° C. for twelve hours and was in the range 1000° C. to 1125° C. for all but about 45 minutes of this time. The reaction mass was cooled in an atmosphere of chlorine. A further 100 grams were chlorinated similarly, actual temperature was in excess of 800° C. for eleven and three quarter hours and was in the range 1000° C. to 1125° C. for ten hours with one period of twenty minutes during which temperature varied from 1150° C. to 1170° C. This reaction mass was also cooled in a chlorine atmosphere. The two reaction masses were combined and the chlorination was continued using a flow rate of dried chlorine in excess of 12 grams per minute; actual temperature was in excess of 800° C. for twelve and a half hours and was in the range 1000° C. to 1125° C. for eleven hours. The reaction mass was dechlorinated by heating in the laboratory oven at 110–120° C. A photomicrograph of the resulting mineral active carbon product at 330× magnification is reproduced here as Figure 1 of the accompanying drawings. The reflected light shows a typical laminated structure.

#### EXAMPLE No. 6.

(For electron photomicrograph at 37350× magnification showing lamellar structure, i.e. Figures 2 and 3).

100 grams of abrasive grade 16 grit black silicon carbide (nominally 99% SiC) were placed in a 1" diameter mullite tube provided with an external electric heater and chlorine was passed through the tube at a rate of 10–11 grams per minute while maintaining a nominal temperature of 800° C. Temperature was in the range 760°–840° C. for a total of one hundred and thirty-six hours during which time the reaction mass was stirred from time to time. After cooling in an atmosphere of chlorine the carbon was dechlorinated by heating overnight in a laboratory oven at 120° C. The resulting mineral active carbon contained 3.2% ash. A finely ground sample of the mineral active carbon under the electron microscope at



37350× magnification is shown here as Figures 2 and 3. Figure 2 shows the shingle-like appearance of the typical lamellar structure when viewed on the flat, and Figure 3 shows a typical edge view of this lamellar structure.

#### EXAMPLE NO. 7.

(Summarized in Table 1 below).

100 grams of abrasive grade 16 grit black silicon carbide (nominally 99% SiC) were placed in a one inch diameter mullite tube provided with an external electric heater and chlorine was passed through the tube at a rate of 10 to 12 grams per minute while maintaining a nominal temperature of 1050° C. Actual temperature was in excess of 800° C. for periods of time totalling fourteen and one half hours of which ten and one half hours were in the 1000° C. to 1150° C. range. A further 100 grams were chlorinated similarly; actual temperature was in excess of 800° C. for nine and one half hours of which eight hours were in the range 1000° C. to 1150° C. A third lot of 100 grams were chlorinated similarly; actual temperature was in excess of 800° C. for ten hours of which eight hours were in the range 1000° C. to 1150° C. The second and third lots and part of the first lot were then combined and the chlorination was continued in a 1.5 inch diameter mullite tube; actual temperature was in excess of 800° C. for twenty-three hours of which eighteen and a half hours were in the range 1000° C. After cooling in an atmosphere of chlorine the carbon was dechlorinated by heating overnight in the laboratory oven at 120° C. The resulting mineral active carbon contained 2.3% ash in which no unreacted silicon carbide was visible; the ash was white, indicating the absence of iron impurities.

Part of this mineral active carbon was crushed and screened through 150 mesh, part was ground and screened through 325 mesh and part was left in its original form. These samples were tested as follows, the results being summarized in Table 1 below:

#### Ash

About 0.2 gram of the 150 mesh mineral active carbon was heated in a porcelain crucible over a Meker burner until ashing was complete; the ash was found to be 2.5% of the original sample weight.

#### Electrical Resistivity

About 3 grams of the 150 mesh mineral active carbon was placed in a ceramic cylinder, 6.4 cm. long and 3.4 cm. inside diameter, which was fitted with copper plungers. A pressure of 2000 pounds per square inch was exerted on the carbon by compressing the plungers between the insulated platens of a laboratory press. The linear

dimension of the carbon column was obtained by a micrometer and the resistance was measured by an ohmmeter connected to the copper plungers. From the observed values the electrical resistivity of the carbon under 2000 pounds per square inch pressure was calculated to be 0.044 ohm-cms.

#### Gas Adsorption Capacity—Chlorine

About 0.2 gram of the 150 mesh mineral active carbon, dried for 2 hours at 110° C. was weighed into a 9 mm. × 10 mm. Pyrex glass tube, in which it was supported on glass wool, and chlorine gas was passed through the sample at 100 millilitres per minute flow rate until the heat of adsorption had dissipated and the tube reached constant weight. The weight of chlorine adsorbed, after correcting the final weighing for the weight of the chlorine atmosphere in the tube, was 0.580 gram per gram of sample.

#### Vapour Adsorption Capacity—

##### Acetone, Benzene, m-Xylene, Water

About 0.2 gram of the 150 mesh mineral active carbon, carbon, dried for 2 hours at 110° C. was placed in the 9 × 100 mm. adsorption tube. Air was bubbled through the test liquid (acetone, benzene, m-xylene, or water) at room temperature at 100 millilitres per minute rate and then through the carbon sample at room temperature until a constant weight was attained, except that in the case of water the test was arbitrarily terminated after two hours. The weights of the various vapours adsorbed were:—

Acetone	0.321 gram per gram of sample, at saturation	
Benzene	0.403 gram per gram of sample, at saturation	100
m-Xylene	0.377 gram per gram of sample, at saturation	
Water	0.169 gram per gram of sample, after two hours	105

#### Heat of Wetting—

##### Acetone, Benzene, m-Xylene, Water

A glass tube 30 mm. × 180 mm. fitted with a nichrome wire manual stirrer, was suspended in a glass jacket which was surrounded by water at 25° C., within a Dewar flask. Twenty millilitres of the test liquid was pipetted into the glass tube and a sample container with a weighed sample of 150 mesh carbon was supported at the lip of the glass tube. The bulb of a Beckmann thermometer was immersed in the test liquid and readings were taken to the nearest 0.001° C. When the temperature of the calorimeter became constant, the weighed carbon sample was added rapidly to the test liquid, stirred, and the resulting temperature change was recorded. The measured heats of wetting were:—



In acetone 11.1 calories per gram of sample  
 In benzene 10.6 calories per gram of sample  
 In *m*-xylene 10.8 calories per gram of sample  
 In water 6.5 calories per gram of sample

#### 5 *Adsorption from Aqueous Solution—Iodine*

About 0.2 gram of 325 mesh carbon was weighed into a 250 ml. conical flask and 10 ml. of 0.7 molar HCl was added. The mixture was heated to boiling and cooled; then 10 40 ml. of N/10 iodine solution was added. The flask was shaken mechanically for forty minutes, the carbon was allowed to settle, a 10 ml. aliquot was withdrawn by pipette and titrated with N/10 sodium thiosulphate 15 solution. The iodine which had disappeared from solution by adsorption on the carbon was found by calculation to be 1.230 grams per gram of sample.

#### 20 *Adsorption from Aqueous Solution—Phenol*

50 milligrams of the 325 mesh carbon were weighed into a 250 ml. conical flask and 100 ml. of 1.00 gram per litre phenol solution were added by pipette. The flask was shaken mechanically for one hour, the 25 carbon was allowed to settle, and a 20 ml. aliquot was transferred to a second flask followed by 20 ml. of N/10 potassium bromate solution containing 8.7 grams per litre of sodium bromide and by 5 ml. of concentrated hydrochloric acid. After the precipitate of tribromophenol had formed, 10 30 ml. of 5% potassium iodide solution was added. The liberated iodine was titrated with N/10 sodium thiosulphate and the 35 amount of phenol which had disappeared from solution by adsorption on the carbon was found by calculation to be 0.344 gram per gram of carbon.

#### 40 *Adsorption from Aqueous Solution—*

##### *Methylene Blue*

A 0.200 gram sample of 325 mesh carbon was placed in a 250 ml. conical flask and 80 ml. of aqueous methylene blue solution containing 1.000 gram of methylene blue per 45 litre was pipetted into the flask. It was shaken mechanically for one hour, the carbon allowed to settle and a 1 ml. aliquot was pipetted into a 20 mm. test tube where 20 ml. of water was added. Concentration of 50 this dilute solution of methylene blue was determined by visual comparison with similar sealed tubes of known methylene blue concentration. The methylene blue which had disappeared from solution by adsorption on 55 the carbon was found to be 0.336 gram per gram of sample.

#### *Hydrogen*

The sample of uncrushed carbon was dried at 200° C. and then burned with oxygen in a 60 combustion train while collecting the water, formed by combustion of any contained

hydrogen, in an absorption tower. It was found that the mineral active carbon contained 0.00% hydrogen, that is, no hydrogen was present as part of the mineral active carbon, as distinguished from adsorbed 65 water which, of course, contains hydrogen.

#### *pH*

Approximately 0.2 gram of 325 mesh carbon was added to 5 ml. of distilled water, heated to boiling, then cooled to room temperature. The pH of the solution was determined using a Beckmann pH meter and found to be 2.4. 70

#### *X-Ray Diffraction*

A sample of the 325 mesh mineral active carbon was examined by X-ray diffraction using the K radiation from a copper target. The X-ray tube current was 20 milliamperes and voltage was 30 K. The spectrum was scanned at a rate of 1° per second through a scanning angle (2 $\theta$ ) range of at least 10° to 90° with a full scale counting rate of 240 counts per second. The (002) line was weak and diffuse, corresponding to about two aromatic planes only in the crystallites. The 85 (10) line was diffuse and just perceptible. There was not trace of a (11) line. In general the aromatic crystalline pattern was much weaker than for a hard coke heat treated 90 at 1400° C.

#### *Electron Photomicrograph*

A finely ground sample of the mineral active carbon, when examined under the electron microscope at magnifications of 95 37350 $\times$  and 82250 $\times$  showed a well developed lamellar structure.

#### *Optical Photomicrograph*

An unground sample of the granular mineral active carbon under an ordinary 100 microscope at 330 $\times$  magnification showed a laminated structure.

#### *Magnetic Resonance*

A sample of the mineral active carbon was tested for paramagnetic electron spin resonance using a spectrometer capable of detecting adsorption lines less than 100 Gauss in width and of an intensity greater than 10<sup>17</sup> free spins per gram. The sample was first examined in air, then under vacuum. 105 It was heated to 450° C. under vacuum, cooled to room temperature and again examined under vacuum; it was similarly heat treated at 1200° C., 1400° C. and 1600° C. and examined under vacuum at room tem- 115 perature. A very small magnetic resonance line was detectable at 1600° C. but no lines were observed below this heat treatment temperature.

EXAMPLE No. 8.  
(Summarized in Table 1 below).

100 grams of abrasive grade 16 grit black silicon carbide (nominally 99% SiC) were placed in a one inch diameter mullite tube provided with an external electric heater and chlorine was passed through the tube at a rate of 10 to 12 grams per minute while maintaining a nominal temperature of 1200° C. Actual temperature was in excess of 800° C. for periods of time totalling twelve and three quarter hours of which ten and three quarter hours were in the range 1150° C. to 1250° C. Only once did the temperature exceed 1250° C. during the run when 1280° C. was recorded briefly. After cooling in an atmosphere of chlorine the carbon was dechlorinated by heating overnight in a laboratory oven at 120° C.

Part of this mineral carbon was crushed and screened through 150 mesh, part was ground and screened through 325 mesh, and part was left in its original form. These samples were tested as described for Example 7; the values obtained are shown in Table 1 below.

A sample of the 325 mesh mineral active carbon was examined by X-ray diffraction as described for Example 7; the aromatic crystalline pattern was essentially identical with that obtained for Example 7, being much weaker than for a hard coke heat treated at 1400° C.

A finely ground sample of the mineral active carbon, when examined under the electron microscope at magnification of 37500× and 82250×, showed a well developed lamellar structure.

An unground sample of the granular mineral active carbon under an ordinary microscope at 330× magnification showed a laminated structure.

EXAMPLE No. 9.  
(Summarized in Table 1 below).

250 grams of abrasive grade 16 grit black silicon carbide (nominally 99% SiC) were placed in a 1.5 inch diameter mullite tube provided with an external electric heater and chlorine was passed through the tube at a rate of 10 to 11 grams per minute. Twenty minutes after the temperature had first reached 800° C. a temperature in excess of 1300° C. was noted, then both the thermocouple and the electric heater failed. It was subsequently found that the mullite reaction tube and the mullite thermocouple protection tube had melted (M.P. about 1650° C.). The chlorine flow was maintained and reaction continued at white heat for some time, gradually subsiding till the red glow disappeared, after which the temperature fell rapidly. The product, which was fairly well

carbonized, was placed in a new tube and chlorinated at 950—1050° C. for three and a half hours. It was then decided to terminate the chlorination so that the carbon would be substantially all formed at approximately 1650° C. It was cooled in chlorine and dechlorinated by heating in a laboratory oven over-night at about 110° C. The product contained 28.9% ash, most of which was unreacted silicon carbide.

Part of this mineral active carbon was crushed and screened through 150 mesh, part was ground and screened through 325 mesh, and part was left in its original form. These samples were tested as described for Example 7 and the observed values were then adjusted to a contained carbon basis using the ash determination on the 150 mesh material; the values obtained are shown in Table I below. Because of the contained silicon carbide, electrical resistivity of this sample has no significance.

A sample of the 325 mesh mineral active carbon was examined by X-ray diffraction as described for Example 7; the aromatic crystalline pattern showed a weak but well defined (002) line, a just perceptible, diffuse (10) line, but no (11) line; this pattern was similar to that for a hard coke at 1400° C. except that the (10) line of the mineral active carbon was noticeably weaker.

A finely ground sample of the mineral active carbon, when examined under the electron microscope at a magnification of 37350, showed a well developed lamellar structure.

EXAMPLE No. 10.  
(Summarized in Table I below).

70 grit abrasive grade black silicon carbide (nominally 99% SiC) was placed in a 17 mm. diameter Vycor tube provided with an external electric heater. The tube was flushed with chlorine at room temperature for 15 minutes then raised to 1050° C. for 24 hours while continuing the chlorine flow. The chlorine flow was stopped and the reaction product was purged and dechlorinated by eight cycles of cooling to room temperature and reheating to 1050° C. while maintaining a slow flow of nitrogen through the Vycor tube. The chlorine and the nitrogen used in this example were dried by bubbling through concentrated sulphuric acid.

Part of the resulting mineral active carbon was crushed and screened through 150 mesh, part was ground and screened through 325 mesh, and part was left in its original form. These samples were tested as described for Example 7; the values obtained are shown in Table I below.

A sample of the 325 mesh mineral active carbon was examined by X-ray diffraction as described for Example 7; the (002) line

was barely perceptible but the (10) and (11) lines were absent.

5 A finely ground sample of the mineral active carbon, when examined under the electron microscope at a magnification of 37350, showed a well developed lamellar structure.

10 An unground sample of the granular mineral active carbon under an ordinary microscope at 330 $\times$  magnification showed a laminated structure.

#### EXAMPLE No. 11.

(Summarized in Table I below).

15 70 grit abrasive grade green silicon carbide (nominally 99.5% SiC) was placed in a 17 mm. Vycor tube provided with an external electric heater. The tube was flushed with chlorine at room temperature for 15 minutes then raised to 825° C. for 630 hours while  
20 continuing the chlorine flow. During the early part of the run hot spots were controlled by diluting the chlorine feed with nitrogen as well as by decreasing the heat supplied by the external electric heaters.  
25 The chlorine flow was stopped and the reaction product was purged and dechlorinated by eight cycles of cooling to room temperature and reheating to 825° C. while maintaining a slow flow of nitrogen through the  
30 Vycor tube. The chlorine and the nitrogen used in this example were dried by bubbling through concentrated sulphuric acid. Part of the resulting mineral active carbon was crushed and screened through 150 mesh, part  
35 was ground and screened through 325 mesh, and part was left in its original form. These samples were tested as described for Example 7 except that the sample was dried  
40 at 300° C. before the hydrogen determination; the values obtained are shown in Table I below. A sample of the carbon withdrawn from the reaction tube after cooling in nitrogen but before the cyclic purging operation had a pH value of 2.4.

45 A sample of the 325 mesh mineral active carbon was examined by X-ray diffraction as described for Example 7; the (002) line was barely perceptible but the (10) and (11) lines were absent.

50 A finely ground sample of the mineral active carbon, when examined under the electron microscope at magnifications of 37500 $\times$  and 82250 $\times$  showed a well developed lamellar structure.

55 An underground sample of the granular mineral active carbon under an ordinary microscope at 330 $\times$  magnification showed a laminated structure.

60 A sample of the mineral active carbon was tested for paramagnetic electron spin resq-

nance using a spectrometer capable of detecting absorption lines less than 100 Gauss in width and of an intensity greater than 10<sup>17</sup> free spins per gram. The sample was examined first in air, then under vacuum. It  
65 was heated to 450° C. under vacuum, cooled to room temperature and again examined under vacuum; it was similarly heat treated at 750° C., 900° C., 1070° C., 1200° C.,  
70 1400° C., and 1600° C., and examined under vacuum at room temperature. In none of these cases was any electron spin resonance absorption detectable.

#### EXAMPLE No. 12.

110 grams of abrasive grade 8 grit black  
75 silicon carbide (nominally 99% SiC) were placed in a one inch diameter mullite tube provided with an external electric heater and chlorine was passed through the tube at a rate of 10 to 12 grams per minute while  
80 maintaining a nominal temperature of 1050° C. Actual temperature was in excess of 800° C. for thirty-seven hours of which thirty-one hours was in the range 1000° C.—1120°  
85 C. After cooling in an atmosphere of chlorine the carbon was dechlorinated by heating overnight in a laboratory oven at 120° C. The resulting mineral active carbon contained 0.4% ash.

#### EXAMPLE No. 13.

90 About 25 grams of abrasive grade 240 grit green silicon carbide (nominally 99.5% SiC) were placed in a porcelain boat in a one inch diameter silica tube provided with an external electric heater and chlorine was passed  
95 through the tube at a rate of about 0.465 gram per minute, while maintaining a temperature of 900° C. at a thermocouple in a Vycor protection tube in the gas stream just above the boat, for a total of 325 minutes.  
100 Oxygen-free, thoroughly dried nitrogen was used to sweep out the tube (a) before the chlorination while the tube was being raised to temperature, and (b) after the chlorination while the tube was cooling to below 500° C.  
105 The silicon tetrachloride produced was condensed in a tube cooled in ice. The resulting mineral active carbon contained 6.2% ash. Upon pumping under vacuum for 30 minutes at 150° C. the mineral active carbon lost  
110 6.7% in weight and then was able to adsorb 0.635 gram of chlorine per gram of sample at 30° C. This sample of mineral active carbon adsorbed 0.913 gram of iodine per  
115 gram of sample from aqueous iodine-potassium iodide solution. Half a gram of this sample adsorbed 99.93% of the methylene blue from an aqueous solution containing 0.500 gram of methylene blue in 75 ml. of water when they were shaken together for  
120 60 minutes.

## EXAMPLE NO. 14.

(Preparation of Mineral Active Carbon for use in Dechlorination Examples Nos. 16 to 18 and 24).

5 100 grams of abrasive grade 16 grit black silicon carbide (nominally 99% SiC) were placed in a one inch mullite tube provided with an external electric heater and chlorine was passed through the tube at a rate of 10 to 12 grams per minute while maintaining a nominal temperature of 1050° C. Actual temperature was in excess of 800° C. for periods of time totalling forty-seven hours of which forty-five hours were in the 1000° C. to 1150° C. range; the reaction once ran away reaching a temperature of 1350° C. but was immediately brought under control by introducing nitrogen into the system, the total time at temperatures in excess of 1180° C. being less than three minutes. The product was cooled to room temperature in an atmosphere of chlorine. A sample of the product, after dechlorination, showed 2.5% ash.

## EXAMPLE NO. 15.

(Preparation of Active Carbon for use in Dechlorination Examples Nos. 19 to 23 and 25 to 37).

30 100 grams of abrasive grade 16 grit black silicon carbide (nominally 99% SiC) were placed in a one inch mullite tube provided with an external electric heater and chlorine was passed through the tube at a rate of 14 to 15 grams per minute while maintaining a nominal temperature of 1050° C. Actual temperature was in excess of 800° C. for seventeen hours of which fifteen hours were in the 1000° C. to 1150° C range. The product was cooled to room temperature in an atmosphere of chlorine. A sample of the product was dechlorinated at 120° C. for an ash determination which showed 3.4% ash.

EXAMPLE NO. 16.  
(Static Dechlorination).

45 A sample of mineral active carbon from Example 14, containing 0.326 gram of chlorine per gram of carbon was placed in a sample tube open at one end only and heated at 210° C. without any flow of gas through the sample until the sample was completely dechlorinated. Grams of chlorine still adsorbed on 0.2523 gram of carbon after various heating intervals were as follows:—

Time of Dechlorination at 210° C.	Chlorine Still Adsorbed
Initial	0.0824 gram
15 minutes	0.0070 gram
30 minutes	0.0006 gram
45 minutes	0.0002 gram

## EXAMPLE NO. 17.

(Static Dechlorination).

A sample of mineral active carbon from Example 14 containing 0.581 gram of chlorine per gram of carbon was placed in a sample tube open at one end only and heated at 250° C. without any flow of gas through the sample until the sample was completely dechlorinated. Grams of chlorine still adsorbed on 0.2403 gram of carbon after various heating intervals were as follows:—

Time of Dechlorination at 250° C.	Chlorine Still Adsorbed	
Initial	0.1396 gram	
15 minutes	0.0129 gram	75
30 minutes	0.0049 gram	
45 minutes	0.0012 gram	
60 minutes	0.0003 gram	
75 minutes	0.0001 gram	
90 minutes	0.0000 gram	80

## EXAMPLE NO. 18.

(Airstream Dechlorination at 175° C.).

A sample of mineral active carbon from Example 14 containing 0.635 gram of chlorine per gram of carbon was placed in a sample tube and heated at 175° C. while passing through it air, which had been dried by passing over silica gel and fused caustic soda pellets, until the sample was completely dechlorinated. Grams of chlorine still adsorbed on 0.1994 gram of carbon after various heating intervals were as follows:—

Time of Dechlorination at 175° C.	Chlorine Still Adsorbed	
Initial	0.1069 gram	95
15 minutes	0.0034 gram	
30 minutes	0.0018 gram	
45 minutes	0.0012 gram	
60 minutes	0.0008 gram	
75 minutes	0.0004 gram	100
90 minutes	0.0002 gram	

## EXAMPLE NO. 19.

(Airstream Dechlorination at Room Temperature).

A sample of mineral active carbon from Example 15 containing 0.590 gram of chlorine per gram of carbon was placed in a sample tube at room temperature and air, which had been dried by passing over silica gel and fused caustic soda pellets, was passed through it until the sample was substantially dechlorinated. Grams of chlorine still adsorbed on 0.2209 gram of carbon after various intervals were as follows:—

	Time of Dechlorination at Room Temperature	Chlorine Still Adsorbed
	Initial	0.1303
	3 hours	0.0102
5	6 hours	0.0062
	9 hours	0.0040
	12 hours	0.0023
	16 hours	0.0014
	20 hours	0.0007

10                   EXAMPLE No. 20.  
(Airstream Dechlorination at 150° C.).

15                   A 0.2018 gram sample of undechlorinated mineral carbon from Example 15 was placed in a tube through which was passed air which had been dried by passing over silica gel and fused caustic soda pellets, and the sample was heated at 150° C., until there was no further loss in weight which was for a total of 100 minutes, and heating was continued for a further 30 minutes. The temperature was then raised to 900° C. while passing dry nitrogen through the sample and then through 5% caustic analysis of the caustic for hypochlorite ion showed that no further chlorine had been desorbed from the mineral active carbon at 900° C. The mineral active carbon was then ashed by passing oxygen through the sample tube and adsorbing the products of combustion in 5% caustic soda; no chlorine was evolved from the mineral active carbon when it was ashed. A sample of this same mineral carbon after dechlorination at 150° C. for 100 minutes had a pH value of 2.9, an iodine capacity of 2.03 grams of iodine per gram of sample, and a *m*-xylene capacity of 0.605 gram per gram of sample.

20                   EXAMPLE No. 21.  
(Nitrogen Dechlorination at 150° C.).

40                   A 0.2989 gram sample of undechlorinated mineral carbon from Example 15 was placed in a tube through which was passed nitrogen which had been dried by bubbling through concentrated sulphuric acid, and the sample was heated at 150° C., until there was no further loss in weight, which was for a total of fifty minutes. Treatment at 900° C. and ashing, as described for Example 20, showed that no chlorine remained adsorbed on the carbon. A separate sample dechlorinated 85 minutes in a nitrogen stream at 150° C. had a pH value of 2.4 an iodine capacity of 2.02 grams of iodine per gram of sample, and a *m*-xylene capacity of 0.583 gram per gram of sample.

50                   EXAMPLE No. 22.  
(Steam Dechlorination at 150° C.).

A 0.1690 gram sample of undechlorinated

mineral carbon from Example 15 was placed in a tube through which was passed steam at 150° C. for fifty minutes. Treatment at 900° C. and ashing, as described for Example 20, showed that no chlorine remained adsorbed on the carbon. A separate sample dechlorinated eighty minutes with steam at 150° C. had a pH value of 3.0, an iodine capacity of 2.02 grams of iodine per gram of sample, and a *m*-xylene capacity of 0.607 gram per gram of sample.

70                   EXAMPLE No. 23.  
(Carbon Dioxide Dechlorination at 150° C.).

A 0.1740 gram sample of undechlorinated mineral carbon from Example 15 was placed in a tube through which was passed carbon dioxide at 150° C. for fifty minutes; at the end of the first ten minutes the sample had reached constant weight. Treatment at 900° C., and ashing, as described for Example 20, showed that no chlorine remained adsorbed on the carbon. A separate sample dechlorinated thirty minutes with carbon dioxide at 150° C. had a pH value of 2.6, an iodine capacity of 0.188 gram of iodine per gram of sample, and a *m*-xylene capacity of 0.610 gram per gram of sample.

85                   EXAMPLE No. 24.  
(Vacuum Dechlorination).

About 0.2 gram samples of mineral active carbon from Example 14 were dechlorinated by evacuation at 20 mm. mercury at temperatures and for times shown in Table III below; this table records the chlorine adsorbed on the carbon before and after dechlorination. Dechlorination was substantially complete at 0° C. after twelve to fifteen hours; dechlorination was complete at 25° C. after five to six hours.

90                   EXAMPLE No. 25.  
(Dechlorination by Water Wash).

A 1.5 gram sample of undechlorinated mineral carbon from Example 15 was washed by passing through it at a rate of about 200 millilitres per minute tap water having a pH of 7.5. After two litres of water had been passed through the carbon the pH value of the carbon was 2.4; after ten litres of water had been passed through the carbon the pH value of the carbon was 6.6 The carbon was then dried at 100° C. for one and a half hours; the mineral active carbon product then had a pH value of 7.3. The mineral active carbon was then analyzed for adsorbed chlorine and for chloride as follows: A sample of the dry mineral active carbon was placed in a tube furnace and heated in a stream of nitrogen at 900° C. for fifteen minutes, the nitrogen stream being

bubbled through 5% caustic soda. Analysis of the caustic solution for hypochlorite showed that no adsorbed chlorine had remained on the mineral active carbon after washing and drying; this analysis showed only a trace of volatile chlorides removed from the mineral active carbon at 900° C. amounting to less than 0.01% of the carbon by weight when expressed as chloride ion.

The sample of mineral active carbon was then ashed by passing air through the tube at 900° C. the off gas being bubbled through 5% caustic soda as before. Analysis of the caustic solution showed that no free chlorine was liberated by ashing and less than 0.01% chloride. The ash residue amounted to 2.9% of the mineral active carbon; analysis of this ash showed no free chlorine and less than 0.001% chloride expressed as percent of the mineral active carbon sample. The iodine adsorption capacity of the mineral active carbon was found to be 1.339 grams of iodine per gram of sample; the *m*-xylene capacity was 0.567 gram per gram of sample. These results are summarized in Table II below.

#### EXAMPLE No. 26.

(Dechlorination with 5% Caustic Soda).

A 1.5 gram sample of undechlorinated mineral carbon from Example 15 was mixed with 20 millilitres of 5% sodium hydroxide solution and heated to boiling. The carbon was then washed by passing tap water through it at a rate of about 200 millilitres per minute; after six litres of water had been passed through the carbon the pH value of the carbon was 8.0. The carbon was then dried at 100° C. for one and a half hours; the mineral active carbon product then had a pH value of 8.4. Analysis of the mineral active carbon product for adsorbed chlorine and for chlorides was carried out as described for Example 25 with results as shown in Table II below. The iodine and *m*-xylene adsorption capacities of the mineral active carbon were found to be as reported in Table II below.

#### EXAMPLE No. 27.

(Dechlorination with 5% Aqueous Ammonia).

About 1.35 grams of undechlorinated mineral carbon from Example 15 was mixed with 20 millilitres of 5% aqueous ammonia and heated. The carbon was then washed by passing tap water through it at a rate of about 200 millilitres per minute; after three litres of water had been passed through the carbon the pH value of the carbon was 7.8. The carbon was then dried at 100° C. for one and a half hours; the mineral active carbon product then had a pH value of 8.1. Analysis of the mineral active carbon pro-

duct for adsorbed chlorine and for chlorides was carried out as described for Example 25 with results as shown in Table II below. The iodine and *m*-xylene adsorption capacities of the mineral active carbon were found to be as reported in Table II below.

#### EXAMPLE No. 28.

(Dechlorination with 5% Caustic Soda followed by HCl).

A 1.5 gram sample of undechlorinated mineral carbon from Example 15 was mixed with 20 millilitres of 5% caustic soda solution and heated to boiling. Then 40 millilitres of 5% hydrochloric acid was added and it was again heated to boiling. The carbon was then washed by passing tap water through it at a rate of about 200 millilitres per minute; after ten litres of water had been passed through the carbon the pH value of the carbon was 7.6. The carbon was then dried at 100° C. for one and a half hours; the mineral active carbon product then had a pH value of 7.3. Analysis of the mineral active carbon product for adsorbed chlorine and for chlorides was carried out as described for Example 25 with results as shown in Table II below. The iodine and *m*-xylene adsorption capacities of the mineral active carbon were found to be as reported in Table II below.

#### EXAMPLE No. 29.

(Dechlorination with 5 Ammonia followed by HCl).

About 1.5 grams of undechlorinated mineral carbon from Example 15 was mixed with 20 millilitres of 5% aqueous ammonia and heated to boiling. Then 40 millilitres of 5% hydrochloric acid was added and it was again heated to boiling. The carbon was then washed by passing tap water through it at a rate of about 200 millilitres per minute; after eleven litres of water had been passed through the carbon the pH value of the carbon was 7.5. The carbon was then dried at 100° C. for one and a half hours; the mineral active carbon product then had a pH value of 7.3. Analysis of the mineral active carbon product for adsorbed chlorine and for chlorides was carried out as described for Example 25 with results as shown in Table II below. The iodine and *m*-xylene adsorption capacities of the mineral active carbon were found to be as reported in Table II below.

#### EXAMPLE No. 30.

(Dechlorination with 5% Sodium Bisulphite).

About 1.5 grams of undechlorinated mineral carbon from Example 15 was mixed with 20 millilitres of 5% aqueous sodium

bisulphite and heated to boiling. The carbon was then washed by passing tap water through it at a rate of about 200 millilitres per minute; after nine litres of water had been passed through the carbon the pH value of the carbon was 7.2. The carbon was then dried at 100° C. for one hour; the mineral active carbon product then had a pH value of 8.2. Analysis of the mineral active carbon product for adsorbed chlorine and for chlorides was carried out as described for Example 25 with results as shown in Table II below. The iodine and *m*-xylene adsorption capacities of the mineral active carbon were found to be as reported in Table II below.

#### EXAMPLE No. 31.

(Dechlorination with 5% Sodium Hyposulphite  $\text{Na}_2\text{S}_2\text{O}_4$ ).

About 1.5 grams of undechlorinated mineral carbon from Example 15 was mixed with 20 millilitres of 5% aqueous sodium hyposulphite ( $\text{Na}_2\text{S}_2\text{O}_4$ ). The carbon was then washed by passing tap water through it at a rate of about 200 millilitres per minute; after eight litres of water had been passed through the carbon the pH value of the carbon was 7.3. The carbon was then dried at 100° C. for one hour; the mineral active carbon product then had a pH value of 2.5. Analysis of the mineral active carbon product for adsorbed chlorine and for chlorides was carried out as described for Example 25 with results as shown in Table II below. The iodine and *m*-xylene adsorption capacities of the mineral active carbon were found to be as reported in Table II below.

#### EXAMPLE No. 32.

(Dechlorination with 5% Sodium Thiosulphate  $\text{Na}_2\text{S}_2\text{O}_3$ ).

About 1.0 gram of undechlorinated mineral carbon from Example 15 was mixed with 20 millilitres of 5% aqueous sodium thiosulphate ( $\text{Na}_2\text{S}_2\text{O}_3$ ). The carbon was then washed by passing tap water through it at a rate of about 200 millilitres per minute; after nineteen litres of water had been passed through the carbon the pH value of the carbon was 7.0. The carbon was then dried at 100° C. for one hour; the mineral active carbon product then had a pH value of 2.4. Analysis of the mineral active carbon product for adsorbed chlorine and for chloride was carried out as described for Example 25 with results as shown in Table II below. The iodine and *m*-xylene adsorption capacities of the mineral active carbon were found to be as reported in Table II below.

#### EXAMPLE No. 33.

(Dechlorination with 5% Hydrogen Peroxide).

About 1.0 gram of undechlorinated mineral active carbon from Example 15 was

mixed with 20 millilitres of 5% hydrogen peroxide solution. The carbon was then washed by passing tap water through it at a rate of about 200 millilitres per minute; after five litres of water had been passed through the carbon the pH value of the carbon was 7.5. The carbon was then dried at 100° C. for one hour; the mineral active carbon then had a pH value of 7.5. Analysis of the mineral active carbon product for adsorbed chlorine and for chloride was carried out as described for Example 25 with results as shown in Table II below. The iodine and *m*-xylene adsorption capacities of the mineral active carbon were found to be as reported in Table II below.

#### EXAMPLE No. 34.

(Dechlorination with 5% Sodium Carbonate).

About 1.0 gram of undechlorinated mineral active carbon from Example 15 was mixed with 20 millilitres of 5% sodium carbonate solution. The carbon was then washed by passing tap water through it at a rate of about 200 millilitres per minute; after one litre of water had been passed through the carbon the pH value of the carbon was 7.6. The carbon was then dried at 100° C. for one hour; the mineral active carbon then had a pH value of 7.8. An analysis of the mineral active carbon product for adsorbed chlorine and for chloride was carried out as described for Example 25 with results as shown in Table II below. The iodine and *m*-xylene adsorption capacities of the mineral active carbon were found to be as reported in Table II below.

#### EXAMPLE No. 35.

(Dechlorination with 5% Sodium Bicarbonate).

About 1.0 gram of undechlorinated mineral active carbon from Example 15 was mixed with 20 millilitres of 5% sodium bicarbonate solution. The carbon was then washed by passing tap water through it; after ten litres of water had been passed through the carbon the pH value of the carbon was 7.3. The carbon was then dried at 100° C. for one hour; the mineral active carbon then had a pH value of 7.7. An analysis of the mineral active carbon product for adsorbed chlorine and for chloride was carried out as described for Example 25 with results as shown in Table II below. The iodine and *m*-xylene adsorption capacities of the mineral active carbon were found to be as reported in Table II below.

#### EXAMPLE No. 36.

(Dechlorination with 5% Hydrochloric Acid).

About 1.0 gram of undechlorinated mineral active carbon from Example 15 was mixed with 20 millilitres of 5% hydrochloric



acid. The carbon was then washed by passing tap water through it; after twenty-one litres of water had been passed through the carbon the pH value of the carbon was 7.3. The carbon was then dried at 100° C. for one hour; the mineral active carbon then had a pH value of 7.8. An analysis of the mineral active carbon product for adsorbed chlorine and for chloride was carried out as described for Example 25 with results as shown in Table II below. The iodine and *m*-xylene adsorption capacities of the mineral active carbon were found to be as reported in Table II below.

15                    **EXAMPLE No. 37.**  
(Removal of Chlorides from Carbon by gas stream at elevated temperatures).

20            (37A) Analysis of the carbon of Example 20 (derived from Example 15), after dechlorination in an air stream for 130 minutes at 150° C., showed no adsorbed chlorine but showed 3.34% chlorine.

25            (37B) A sample of the same carbon from Example 15 after dechlorination in an air stream for 100 minutes at 150° C. had a pH of 2.9 and a *m*-xylene capacity of 0.605 gram per gram.

30            (37C) Analysis of a sample of the carbon from Example 15 after dechlorination in a nitrogen stream for 80 minutes at 150° C. showed no adsorbed chlorine but showed 4.15% chloride.

35            (37D) A further sample from Example 15, as disclosed under Example 21, after dechlorination in a nitrogen stream for 85 minutes at 150° C. had a pH of 2.4 and a *m*-xylene capacity of 0.583 gram per gram.

40            (37E) A sample of the carbon from Example 15 was dechlorinated in an air stream for 100 minutes at 350° C. and showed 2.55% chloride. As compared to sample 37A this was a reduction of 0.79% in the chloride content by raising the temperature from 150° C. to 350° C. Sample 37E was further heated in a stream of nitrogen at 900° C. for 30 minutes after which it was found to have a chloride content of only 0.97%. A further sample (37F) from Example 15 after dechlorination in an air stream for 110 minutes at 350° C. had a pH of 3.7 an increase of 0.8 as compared to sample 37A it had a *m*-xylene capacity of 0.632 gram per gram.

55            (37G) A sample of the carbon from Example 15 was dechlorinated in a nitrogen stream for 60 minutes at 350° C. and showed 1.50% chloride. As compared to sample 37C this was a reduction of 2.65% in the

chloride content by raising the temperature from 150° to 350° C. Sample 37F was further heated in a stream of nitrogen at 900° C. for 30 minutes after which it was found to have a chloride content of only 0.48%. A further sample (37H) from Example 15 after dechlorination in a nitrogen stream for 60 minutes at 350° C. had a pH of 4.6, an increase of 2.2 as compared to sample 37D.

These comparisons are summarized in Table IV below.

**EXAMPLE No. 38.**

(Removal of impurities and formation of neutral carbon by heating to 350° C).

About 2 grams of the dechlorinated mineral active carbon from Example 3 was dried for two hours in a laboratory oven at 100° C. to remove moisture adsorbed from the air since it was prepared; the loss in weight was 2.8%. This dried mineral active carbon had a pH of 3.1. About 1 gram of this dried carbon was placed in a porcelain boat and heated in a tube furnace at 350° C. for two hours without flow through the tube; loss in weight was 5.2%. The resulting carbon had a pH of 7.2.

**EXAMPLE No. 39.**

(Mineral Active Carbon from Metallurgical Grade Silicon Carbide).

120 grams of metallurgical grade 14 mesh and finer silicon carbide (nominally 90% SiC) were placed in a one inch diameter mullite tube provided with an external electric heater and chlorine was passed through the tube at a rate of 8.7 grams per minute while maintaining a nominal temperature of 1050° C. Actual temperature was in excess of 800° C. for twenty-three hours of which nineteen hours was in the range 1000° C.—1100° C. After cooling in an atmosphere of chlorine the carbon was dechlorinated by heating overnight in a laboratory oven at 120° C. The resulting mineral active carbon contained 36.6% ash. It had the following adsorption capacities:—

	Gram per gram of product	
Acetone ... ..	0.140	
<i>m</i> -Xylene ... ..	0.145	
Iodine ... ..	0.980	110
Chloride ... ..	0.205	
Methylene Blue ... ..	0.131	

**EXAMPLE No. 40.**

(Mineral Active Carbon from Firesand).

A sample of firesand, which is an electric

furnace byproduct containing about 50% SiC, was screened to separate the on 40 mesh fraction and 100 grams of this coarse fire-sand were placed in a one inch diameter mullite tube provided with an external electric heater and chlorine was passed through the tube at a rate of 8.7 grams per minute while maintaining a nominal temperature of 1050° C. Actual temperature was in excess of 800° C. for thirty-six hours, of which thirty-two and a half hours were in the range 1000° C.—1100° C. After cooling in an atmosphere of chlorine the carbon was dechlorinated by heating overnight in the laboratory over at 120° C. The resulting mineral active carbon contained 33.6% ash. It had the following adsorption capacities:

	Gram per gram of product
Acetone ... ..	0.085
m-Xylene ... ..	0.095
Iodine ... ..	0.835
Chlorine ... ..	0.152
Methylene Blue ... ..	0.164

EXAMPLE No. 41.  
(Mineral Active Carbon from  
Titanium Carbide).

20 grams of titanium carbide (TiC) were placed in a 15 mm. Vycor tube provided with an external electric heater and chlorine was passed through the tube at a rate of about 5 grams per minute while maintaining a temperature of 800—900° C. Clouds of titanium chloride were evolved. After seventy minutes the process was stopped and the resultant carbon was cooled in an atmosphere of chlorine. It was dechlorinated at 110° C. An ash determination showed that the reaction was about 95% complete. It was chlorinated at 700—750° C. for a further 115 minutes, cooled in chlorine and dechlorinated at 115° C. overnight. The resulting mineral active carbon contained 5.25% ash, corresponding to about 99% completion of the reaction if the original carbide were pure.

The mineral active carbon product adsorbed 0.397 gram chlorine per gram of product, 0.514 gram of iodine per gram of product, or 0.192 gram of methylene blue per gram of product.

A sample of the mineral carbon was examined by X-ray diffraction as described for Example 7; there was no trace of any aromatic crystalline pattern although a strong line due to titania impurities occurred at about the location of the (002) line; the identification of this titania line was confirmed by its shape and by the presence of

other titania lines of the correct relative intensities.

A sample of the mineral active carbon was tested under vacuum for paramagnetic electron spin resonance, as described for Example No. 11, in its original condition and after heat treatment at temperatures of 250° C., 750° C., and 1050° C., in no case was any magnetic resonance detectable.

A finely ground sample of the mineral active carbon, when examined under the electron microscope at a magnification of 37350×, showed a well developed lamellar structure.

EXAMPLE No. 42.  
(Mineral Active Carbon from  
Zirconium Carbide).

About 40 grams of 8/20 mesh zirconium carbide (ZrC) were placed in a 15 mm. Vycor tube provided with an external electric heater and chlorine was passed through the tube at a rate of about 5.3 grams per minute while maintaining a temperature of 620 to 730° C. for 100 minutes; zirconium chloride was evolved freely until the end of 90 minutes. The product was cooled in chlorine and dechlorinated at 115° C. overnight. The resulting mineral active carbon contained 28.8% ash, corresponding to about 95.6% completion of the reaction if the original carbide were pure.

The mineral active carbon product adsorbed 0.276 gram of chlorine per gram of product, 0.888 gram of iodine per gram of product, or 0.210 gram of methylene blue per gram of product.

EXAMPLE No. 43.  
Mineral Active Carbon from  
Aluminium Carbide).

About 20 grams of aluminium carbide (Al<sub>4</sub>C<sub>3</sub>) was placed in a 15 mm. Vycor tube provided with an external electric heater and chlorine was passed through the tube at a rate of about 5.3 grams per minute while maintaining a temperature of 560—680° C. for two hours; aluminium chloride was evolved freely for about thirty minutes and slower for a further forty-five minutes. The product was cooled in chlorine and dechlorinated at 115° C. overnight. The resulting mineral active carbon contained 4.2% ash, corresponding to 99% completion of the reaction if the original carbide were pure.

The mineral active carbon product adsorbed 0.398 gram of chlorine per gram of product, 0.635 gram of iodine per gram of product, or 0.258 gram of methylene blue per gram of product.

A sample of the mineral active carbon was examined by X-ray diffraction as described for Example 7; the (002) line was diffuse and

barely perceptible but the (10) and (11) lines were absent.

A sample of the mineral active carbon was tested under vacuum for paramagnetic electron spin resonance, as described for Example No. 11, in its original condition and after heat treatment at temperatures of 400° C., 640° C., 750° C., 800° C., 900° C.; in no case was any magnetic resonance detectable.

A finely ground sample of the mineral active carbon, when examined under the electron microscope at magnifications of 37,350 $\times$  and 87,250 $\times$ , showed a well developed lamellar structure.

EXAMPLE No. 44.  
(Mineral Active Carbon from  
Zirconium Carbonitride).

About 26 grams of zirconium carbonitride was placed in a 15 mm. Vycor tube provided with an external electric heater and chlorine was passed through the tube at a rate of about 5.3 grams per minute while maintaining a temperature of 500–620° C. for about one and a quarter hours; zirconium tetrachloride was initially evolved freely at 125° C. and the temperature was allowed to rise rapidly to 500° C. reaction was complete at the end of 75 minutes. The product was cooled in chlorine and dechlorinated at 115° C. over the weekend. The resulting mineral active carbon contained 19.6% ash.

The mineral active carbon product adsorbed 0.189 gram of chlorine per gram of product, 0.418 gram of iodine per gram of product, or 0.216 gram of methylene blue per gram of product.

A sample of the mineral active carbon was examined by X-ray diffraction as described for Example 7; there was no trace of any aromatic crystalline pattern.

A sample of the mineral active carbon was tested under vacuum for paramagnetic electron spin resonance, as described for Example No. 11, in its original condition and after heat treatment at temperatures of 250° C., 450° C., 650° C., 900° C., 1050° C.; in no case was any magnetic resonance detectable.

A finely ground sample of the mineral active carbon, when examined under the electron microscope at magnifications of 37,350 $\times$  and 82,250 $\times$  showed a well developed lamellar structure.

EXAMPLE No. 45.  
(Mineral Active Carbon from  
Boron Carbide).

About 8 grams of boron carbide ( $B_4C$ ) were placed in a 15 mm. Vycor tube provided with an external electric heater and chlorine was passed through the tube at a

rate of about 5.3 grams per minute while maintaining a temperature of 630–790° C. for two and a half hours; boron trichloride was evolved freely for about one and a half hours, and slowly for a further hour. The product was cooled in chlorine and dechlorinated at 115° C. for about three hours. The resulting mineral active carbon contained 8.1% ash, corresponding to about 98% completion of the reaction if the original carbide were pure.

The mineral active carbon product adsorbed 0.503 gram of chlorine per gram of product, 1.984 gram of iodine per gram of product, or 0.302 gram of methylene blue per gram of product.

A sample of the mineral active carbon was examined by X-ray diffraction as described for Example 7; there was no trace of any aromatic crystalline pattern, but a weak, sharp line due to  $B_4C$  impurity was observed near the normal position of the (002) line.

A sample of the mineral active carbon was tested under vacuum for paramagnetic electron spin resonance as described for Example No. 11, in its original condition and after heat treatment at temperatures of 250° C., 750° C., 900° C., and 1050° C.; in no case was any magnetic resonance detectable.

A finely ground sample of the mineral active carbon, when examined under the electron microscope at magnifications of 37,350 $\times$  and 82,258 $\times$  showed a well developed lamellar structure.

EXAMPLE No. 46.  
(Mineral Active Carbon from  
Zirconium Carbide).

About 31 grams of an 8/20 mesh zirconium carbide ( $ZrC$ ) were placed in a 15 mm. Vycor tube provided with an external electric heater and chlorine was passed through the tube at a rate of about 6 grams per minute; the reaction started initially at a temperature of 150° C.; the temperature rose to 500° C. during the first ten minutes and chlorination proceeded in the range 500–800° C. during a further 45 minutes. The product was cooled in chlorine and dechlorinated at 110° C. for two and a half hours. The resulting mineral active carbon contained 22.6% ash, corresponding to about 96.7% completion of the reaction if the original carbide were pure.

A sample of the mineral active carbon was examined by X-ray diffraction as described for Example 7; there was no trace of any aromatic crystalline pattern.

A sample of the mineral active carbon was tested under vacuum for paramagnetic electron spin resonance, as described for Example No. 11, in its original condition and after heat treatment at temperatures of

250° C., 750° C., 900° C. and 1050° C.; in no case was any magnetic resonance detectable.

A finely ground sample of the mineral active carbon, when examined under the electron microscope at magnifications of 37,350× and 82,250×, showed a well developed lamellar structure.

As is well known in the art, and for the various reasons disclosed above, the constitution and properties of an active carbon are the unique resultant of the particular raw material used and of the particular method employed. The raw materials employed (metal or metalloid carbides or carbonitrides) and the basic processing method (chlorination to release carbon, followed by dechlorination) are unique raw materials and process in the history of the active carbon art. It is, therefore, apparent that the physical structure of mineral active carbons must be unique and that this structure must impart to the mineral active carbons physical properties which distinguish them from all other forms of carbon previously known to the art. This conclusion is confirmed by the observed properties of mineral active carbons in comparison with the properties of all other forms of carbon known to the art.

Examples 11, 41, 43, 44, 45 and 46 show that mineral active carbons prepared from silicon carbide, titanium carbide, zirconium carbide, aluminium carbide, zirconium carbonitride and boron carbide, at temperatures below 900° C., possess no magnetic resonance detectable with a spectrometer which can detect absorption bands up to 100 Gauss in width and of intensities as low as  $10^{17}$  free spins per gram, using microwaves of 9200 megacycles per second frequency. The detection limit of free spin concentration for a given spectrometer varies with the line width. The measurements were made on the spectrometer at the University of Buffalo which has a sensitivity as follows: at a line width of 30 Gauss a concentration of about  $3 \times 10^{19}$  spins per gram can be detected; at 5 Gauss width,  $2 \times 10^{18}$  spins per gram; and at 0.5 Gauss width, about  $10^{17}$  spins per gram. Known carbons have resonance absorption band widths of the order of one half Gauss and intensities of the order of  $2 \times 10^{20}$  free spins per gram. All carbons which are known to the art and which are formed below about 900° C. and not subsequently heat treated above this temperature possess measurable magnetic resonance. Mineral active carbons formed below about 900° C. on the other hand, either possess no magnetic resonance at all or their adsorption line is at least 100 times weaker and/or 20 to 100 times broader than that of known carbons. Not only do mineral active carbons, as produced, possess no measurable magnetic resonance, but no measurable magnetic

resonance is produced in any of them by heat treatments up to 1500° C. This absence of measurable magnetic resonance alone distinguishes mineral active carbons from all forms of carbon known to the art.

All of the so-called "amorphous" forms of carbon known to the art, which have been formed at or heated to temperatures in excess of 400° C., are in fact somewhat crystalline, in that they have sufficiently developed planar aromatic ring structures to show an X-ray diffraction pattern, of which the (002) line, corresponding to the separation of the two dimensional aromatic lattice planes, is the most prominent feature. Examples 41, 44, 45 and 46 show that mineral active carbons formed from titanium, zirconium and boron carbides, and from zirconium carbonitrides at maximum temperatures in the range 600—900° C. exhibit no aromatic X-ray diffraction pattern at all. Examples 11 and 32 show that mineral active carbons prepared from silicon carbide and from aluminium carbide at maximum temperatures in this range exhibit only a barely perceptible indication of aromatic planes. Examples 7, 8, and 10 show that mineral active carbons formed from silicon carbide at temperatures up to 1250° C. have barely perceptible or very weak and diffuse (002) lines, indicating that they have a much less well developed aromatic ring structure than do any other carbons known to the art. These structures are estimated to correspond, at the most, to a thickness of 2 to 3 aromatic layers and a diameter of 10 Angstrom units. Only Example 9 formed at 1650° C. shows a crystalline structure at all comparable to known carbons. Because increasing temperature increases the mobility of the atoms, increased development of planar aromatic structure is normal as heat treatment temperature increases. It is truly remarkable that even at 1650° C. the mineral active carbon of Example 9 shows less aromatic structure than does a typical hard carbon at 1400° C. Mineral active carbons have, therefore, very much smaller turbostratic crystallites than carbons heretofore known to the art, when compared at the same heat treatment temperature; and mineral active carbons prepared at or below about 1000° C. have smaller turbostratic crystallites than have even been encountered before in the art, while some have no detectable turbostratic structure at all.

Inasmuch as hard carbons typically have relatively small turbostratic crystallites which grow only relatively slowly at higher temperatures, mineral active carbons might be classed as extremely hard carbons. Soft carbons, on the other hand, have very well developed turbostratic crystallites even at 1100° C., which grow very readily with increasing temperatures. In this respect the distinction between mineral active carbons

and soft carbons known to the art is very marked. Soft cokes of the prior art, but not hard cokes or carbon blacks of the prior art, show a lamellar structure under the electron microscope, such as that seen in Figs. 2 and 3. When viewed edgewise, the lamellae appear as alternating strips of high and low density; when viewed on the flat, there are areas of different density due to a shingle-like effect where all the lamellae do not extend the same distance towards the edge of the particle. The outline of such particles is characterised by many fairly straight edges when viewed on the flat or by a scalloped effect when the lamellae are viewed edgewise. These effects are only observed when the particles are thin enough at the edges to be semi-transparent and when the particles happen to be so oriented in the electron microscope that these special views of the structure are apparent. Since the spacing of the lamellar sheets is usually of the order of several hundred Angstrom units, this property is only visible in particles having dimensions several times this magnitude. This structure is found in all soft cokes known to the art and in a few active carbons, notably those which have been made from soft cokes such as petroleum coke. This structure occurs because the fluid stage of carbonisation gives the centres of organisation an opportunity to align themselves in parallel planes. This structure is not found in hard cokes of the prior art. It is quite remarkable, then, to note that all of the "extremely hard" mineral active carbons exhibit a well developed lamellar structure, as demonstrated by Examples 6, 7, 8, 9, 10, 11, 41, 43, 44, 45 and 46, and as illustrated by Figures 2 and 3 which are actual photomicrographs of mineral active carbon prepared from silicon carbide at 825° C. Although lamellar structure under the electron microscope is not a unique property of carbons known to the art, it is unique in combination with a mineral turbostratic structure as revealed by X-ray diffraction.

All mineral active carbons made from silicon carbide, as illustrated by Examples 5, 7, 8, 9, 10, and 11, and by Figure 1, showed a laminar or laminated structure at 330× magnification under the ordinary microscope. This relatively macroscopic laminar structure must be distinguished from the ultra high magnification lamellar structure although both have their origin in a basic planar structure which is, however, too coarse to diffract X-rays. The low magnification laminar appearance shows that the carbon has a stratified structure, often resulting in deep parallel cracks in the granule. Such features can only be observed when the carbon granule is large enough to have relatively extensive surface. Of the other metal carbides employed, only the zirconium carb-

ide grains were large enough to permit observation of this stratification. In Example 46 some laminar structure was observed.

The foregoing properties of mineral active carbons distinguish them from all other forms of carbon, whether surface active or not. They have additional properties which distinguish them from all active carbons previously known to the art. As will be obvious from their inorganic origin, and as is confirmed by Examples 7, 8, 9, 10, and 11, mineral active carbons contain no bound hydrogen, while all known active carbons contain measurable amounts of bound hydrogen, which is a legacy of their organic origin.

The electrical resistivity of known commercial active carbons ranges from 0.08 to 0.7 ohm-cms. Low resistivity is a measure of the extent to which the peripheral side chains and hydrogen have been stripped from the aromatic rings during carbonization, and during activation, of organic carbons. It is not surprising then that mineral active carbons prepared at temperatures in excess of 1000° C. have lower resistivities than are observed for active carbons known to the art, since they contain no side chains or hydrogen at all. Examples 7, 8, and 10 show mineral active carbons prepared above 1000° C. having electrical resistivities about half of the lowest value observed in known active carbons. Example 11 shows that mineral active carbon prepared at 825° C. has about ten times the resistivity of those prepared above 100° C.; this greater resistivity is due, not to the presence of side chains, but to the almost total absence of planar aromatic structures which would help to provide an organized path for the flow of electrons, and in which there are pi-electrons with energies near the conduction band.

Table I below summarizes the properties of Examples 7, 8, 9, 10, and 11. The adsorption capacities and heats of wetting of these mineral active carbons for the wide range of adsorbates reported in this table are all comparable to the values obtainable with active carbons known to the art and offered commercially at the present time. Mineral active carbons are therefore demonstrated to be commercially useful for a wide range of gas and vapour phase and of liquid phase adsorption operations. The high heats of wetting relative to active carbons presently in use illustrate their excellent adsorbate retention tenacity. Although the adsorption capacities and heats of wetting of mineral active carbons fall in about the range of values observed for organic active carbons in general, when a number of adsorbates are considered, the pattern of values obtained is found to differ from those of each individual organic active carbon, thereby distinguishing further between mineral active carbons and

organic active carbons known to the art. Thus, as compared to known carbons, Example 10 has a high adsorption capacity for organic vapour and a very high heat of wetting by them, whereas it has a relatively low capacity for water although the heat of wetting by water is better than average.

5 A comparison of Example 10, which was purged, with Example 7, which was prepared at the same temperature but dechlorinated without purging, shows the substantial gain

in heat of wetting and in capacity for organic vapours, which resulted from the purging operation. The improvement in pH effected by the purging operation is illustrated by Example 11 which had a pH of 2.4 before purging (but after dechlorination) and had a pH of 5.2 after purging. It will be noted that Example 10, after purging, had a pH of 7.1 which is essentially perfect neutrality.

The aforementioned Tables I, II, III and IV are presented below.





TABLE II.  
PROPERTIES OF MINERAL ACTIVE CARBON PREPARED BY WET DECHLORINATION METHODS.

Example No.	Dechlorination Method	pH	Volatile at 900° C.		Volatilized during Ashing at 900° C.		Chloride in Ash (1)	% Ash	Adsorption	
			Chlorine (1)	Chloride (1)	Chlorine (1)	Chloride (1)			Iodine gms./gm.	<i>m</i> -xylene gms./gm.
25	Water Wash ...	7.3	0.00	0.34	0.00	0.01	0.001	2.9	1.339	0.567
26	5% NaOH and Water Wash ...	8.4	0.00	0.23	0.00	0.90	0.054	3.0	1.596	0.550
27	5% NH <sub>4</sub> OH and Water Wash ...	8.1	0.00	0.98	0.00	0.14	0.000	2.0	2.230	0.546
28	5% NaOH, 5% HCl, and Water Wash ...	7.3	0.00	0.27	0.00	0.14	0.000	2.6	1.959	0.464
29	5% NH <sub>4</sub> OH, 5% HCl, and Water Wash ...	7.3	0.00	0.68	0.00	0.31	0.001	7.1(2)	1.992	0.555
30	5% NaHSO <sub>3</sub> and Water Wash ...	8.2	0.00	1.12	0.00	0.56	0.200	7.5(2)	1.912	0.574
31	5% Na <sub>2</sub> S <sub>2</sub> O <sub>4</sub> and Water Wash ...	2.5	0.00	1.17	0.00	0.16	0.000	2.9	1.891	0.520
32	5% Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> and Water Wash ...	2.4	0.00	1.29	0.00	0.09	0.001	1.5	1.839	0.478
33	5% H <sub>2</sub> O <sub>2</sub> and Water Wash ...	7.3	0.00	0.85	0.00	0.66	0.000	1.8	1.946	0.412
34	5% Na <sub>2</sub> CO <sub>3</sub> and Water Wash ...	7.8	0.00	1.29	0.00	0.35	0.000	7.5(2)	1.771	0.460
35	5% NaHCO <sub>3</sub> and Water Wash ...	7.7	0.00	0.84	0.00	0.45	0.000	2.5	1.710	0.537
36	5% HCl and Water Wash ...	7.8	0.00	1.47	0.00	0.04	0.000	2.3	1.722	0.529

(1) As percent of mineral active carbon.

(2) High Ash value due to presence of unreacted silicon carbide.

TABLE III.  
VACUUM DECHLORINATION.  
(Data for Example 24).

Initial Sample		Evacuation at 20 mm. Hg		Chlorine Remaining in Carbon		
Carbon Grams	Chlorine Grams	Chlorine as gms./gm. carbon	Temp. ° C.	Time Hrs.	Grams	% of Initial
0.1840	0.1383	0.752	0	5	0.0073	5.3
0.1172	0.1374	0.775	0	8	0.0044	3.2
0.1816	0.1387	0.764	0	15	0.0016	1.2
0.1764	0.1353	0.767	0	11.5	0.0012	0.9
0.1914	0.1113	0.581	25	0.5	0.0097	8.7
0.1884	0.1114	0.591	25	1.5	0.0033	3.0
0.1881	0.1250	0.665	25	3.0	0.0070	5.6
0.1824	0.1234	0.676	25	5.6	0.0000	0.0

TABLE IV.  
REMOVAL OF CHLORIDES BY HEATING IN GAS STREAM.  
(Data of Example 37)

Treatment		Chloride Analysis			Other Properties		
Gas Stream	Temp. ° C.	Example No.	Treatment Time, Mins.	% Cl <sup>-</sup>	Example No.	Treatment Time Mins.	m-xylene gms./gram
Air	150	37A	130	3.34	37B	100	0.605
Air	350	37E	100	2.55	37F	110	0.632
Nitrogen	900	37E		0.97			
Nitrogen	150	37C	80	4.15	37D	85	0.583
Nitrogen	350	36G	60	1.50	37H	60	0.613
Nitrogen	900	37G		0.48			

WHAT I CLAIM IS:—

1. Dechlorinated mineral active carbon containing no bound hydrogen.
2. Mineral active carbon as claimed in Claim 1 having a specific electrical resistivity, when 150 mesh material is under 2000 pounds per square inch pressure, less than 0.050 ohm-cms.
3. Mineral active carbon as claimed in Claim 1 or 2 having a pH in aqueous suspension in the range 5.0 to 8.0.
4. Mineral active carbon as claimed in any of the preceding claims having less than 2.0% inorganic ash.
5. Mineral active carbon as claimed in Claim 4 having less than 1.0% inorganic ash.
6. Mineral active carbon as claimed in any of the preceding claims having no measurable paramagnetic electron spin adsorption at heat treatment temperatures up to 1500° C.
7. Mineral active carbon as claimed in any of the preceding claims distinguished by the essential absence of the X-ray diffrac-

tion pattern which is characteristic of aromatic crystallites.

8. Mineral active carbon as claimed in any of the preceding claims having an ultra high magnification lamellar structure.

9. Dechlorinated mineral active carbon containing no bound hydrogen substantially as herein described with reference to and as illustrated in any of the foregoing examples.

10. A process for producing dechlorinated mineral active carbon containing no bound hydrogen comprising chlorinating, at an elevated temperature, a carbide or carbonitride of a metal or metalloid whose chloride is volatile at said elevated temperature, volatilising and removing the resulting chloride from the reaction mass and dechlorinating the residual carbon.

11. A process as claimed in Claim 10 in which the dechlorination is effected by subjecting the residual carbon to heat.

12. A process as claimed in Claim 11 in which the residual carbon is heated to a temperature of at least 100° C.

13. A process as claimed in Claim 12 in which the residual carbon is heated to a temperature in the range 200—300° C.

14. A process as claimed in Claim 10 in which the dechlorination is effected by subjecting the residual carbon to a vacuum.

15. A process as claimed in Claim 10 in which the dechlorination is effected by subjecting the residual carbon to a stream of gas which does not react with the carbon at the temperature employed.

16. A process as claimed in Claim 15 in which the dechlorination is effected at atmospheric pressure and at a temperature of 150° C.

17. A process as claimed in Claim 15 in which the gas is air, nitrogen, steam or carbon dioxide.

18. A process as claimed in Claim 17 in which the air is dry.

19. A process as claimed in Claim 10 in which the dechlorination is effected by washing the residual carbon with water.

20. A process as claimed in Claim 10 in which the dechlorination is effected by washing the residual carbon with a solution of an alkaline material.

21. A process as claimed in Claim 20 in which the alkaline material is an alkali hydroxide, carbonate or bicarbonate or ammonia.

22. A process as claimed in Claim 20 or 21 in which the washing with the solution of alkaline material is followed by washing with water.

23. A process as claimed in Claim 20 or 21 in which the washing with the solution of alkaline material is followed by neutralisation of the residual alkaline solution and washing with water.

24. A process as claimed in Claim 10 in which the dechlorination is effected by treating the residual carbon with a reducing agent.

25. A process as claimed in Claim 24 in which the reducing agent is an alkali bisulphite, hyposulphite or thiosulphite or hydrogen peroxide.

26. A process as claimed in Claim 24 or 25 in which the treatment with reducing agent is followed by washing with water.

27. A process as claimed in Claim 24 or 25 in which any excess reducing agent is destroyed by means of an oxidising agent and this is followed by washing with water.

28. A process as claimed in Claim 10 in which the dechlorination is effected by treating the residual carbon with a solution of hydrochloric acid.

29. A process as claimed in any of Claims 10 to 28 in which moisture is excluded.

30. A process as claimed in any of Claims 10 to 29 in which the dechlorination is effected before exposure of the carbon to moist air.

31. A process as claimed in any of Claims 10 to 30 in which the rate of reaction is controlled by throttling the chlorine feed rate or by diluting the chlorine with an inert gas.

32. A process as claimed in any of Claims 10 to 31 in which any chloride remaining in the carbon is removed by a cyclic fluctuation in temperature or pressure.

33. A process as claimed in any of Claims 10 to 32 in which the chlorination is effected at a temperature in the range 800° C.—1800° C.

34. A process as claimed in Claim 33 in which the chlorination is effected at a temperature in the range 900° C.—1200° C.

35. A process as claimed in any of Claims 10 to 34 in which the carbide is silicon carbide.

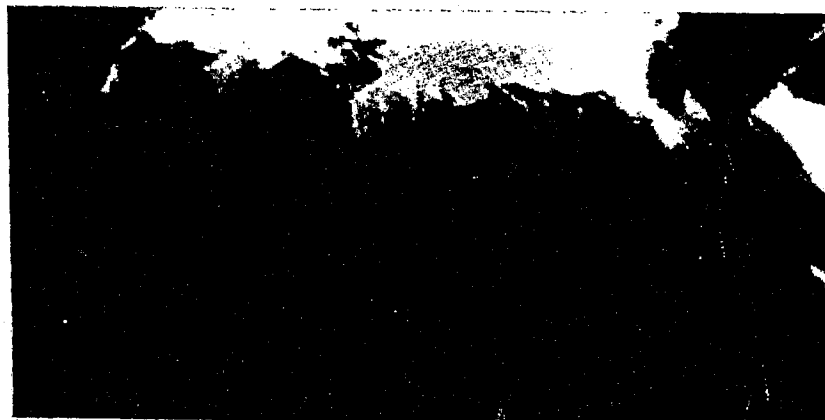
36. A process as claimed in Claim 35 in which the silicon carbide is abrasive grade black silicon carbide or green silicon carbide.

37. A process as claimed in any of Claims 10 to 36 in which the carbide is titanium, zirconium, aluminium or boron carbide.

38. A process as claimed in any of Claims 10 to 36 in which the carbonitride is titanium or zirconium carbonitride.

39. A process for the preparation of dechlorinated mineral active carbon containing no bound hydrogen substantially as herein described, with reference to and as illustrated in any of the foregoing Examples.

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*FIG. 1.**FIG. 2.**FIG. 3.*